Acknowledgment.—The author wishes to thank the Eli Lilly Company for the gift of the crystalline zinc-insulin used in this work, and also gratefully acknowledges the tenure of an Arthur Amos Noyes Fellowship.

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The Action of Raney Nickel on Selenium Compounds[1,2]

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RECEIVED DECEMBER 20, 1954

In connection with our studies of the action of Raney nickel on sulfur compounds we became interested in the behavior of selenium compounds under identical conditions. Since the hydrogenolytic deselenization of such compounds has been described[3] recently, we wish to report our results which were obtained using degassed Raney nickel,[4] thus excluding hydrogen as far as possible. From Table I it can be seen that diselenides and phenyl selenobenzoate are transformed by Raney nickel degassed at 200° into selenides when heated at 80° but that they, as well as diphenyl selenide, yield biphenyl, when the reaction temperature is raised to 180°; a mixture of both reaction products is obtained at 140°. In absence of Raney nickel the selenium compounds are stable in boiling xylene, and melt without decomposition.

TABLE I

TRANSFORMATION OF SELENIUM COMPOUNDS IN PRESENCE OF RANEY NICKEL DEGASSED AT 200°

Starting material	Heated at °C.	Hours	Comp. obtained	Yield, %	M.p. or b.p. (mm.), °C.
Diphenyl diselenide	80[a]	15	Diphenyl selenide	89	130–132 (2)[e]
	140[b]	14.5	Diphenyl selenide +	21[d]	136–142 (4)[e]
			biphenyl	31[d]	68.5–69.5[f]
	180[c]	7	Biphenyl	72	68.9–70[f]
Di-*o*-tolyl diselenide	140[b]	15	Di-*o*-tolyl selenide	67	61–61.5[f]
Phenyl selenobenzoate	80[a]	15	Diphenyl selenide	54	135–140 (3)[e]
	140[b]	15	Diphenyl selenide +	42[d]	137–143 (4)[e]
			biphenyl	15[d]	68–69.5[f]
	180[c]	8.5	Biphenyl	51	69–70[f]
Diphenyl selenide	180[c]	8	Biphenyl	77	69.5–710.5[f]
Di-*o*-tolylselenide	180[c]	8	Di-*o*-tolyl	52	249–250[g]

[a] In benzene. [b] In xylene. [c] Without solvent in a stream of nitrogen. [d] Calculated as recovery of phenyl radicals (see ref. 4b). [e] Identified by transformation into diphenylselenium dibromide, m.p. 134°, dec. about 145°. [f] Identified by mixed m.p. with authentic sample. [g] Identified by oxidation to 2,2′-diphenic acid, m.p. 225–228°.

These selenium compounds behave therefore in presence of degassed Raney nickel in the same manner as do the corresponding sulfur compounds.[4] This is true also for the biphenyl formation, since it has been found that the sulfur compounds also give biphenyl when heated with degassed Raney nickel at 220°.[5] However, selenium is eliminated from the molecule at a lower temperature, since biphenyl formation is completed at 180° and is formed in considerable amounts even in boiling xylene, where diphenyl sulfide is the only product obtained from the sulfur compounds.

It seems that the methyl groups in the *o*-positions make the reaction with the Raney nickel somewhat difficult, since di-*o*-tolyl diselenide yields at 140° only the corresponding selenide and no di-*o*-tolyl. This problem is being investigated on selenium as well as on sulfur compounds.

Acknowledgment.—We wish to express our gratitude to the Conselho Nacional de Pesquisas of Brazil for a fellowship granted to W. F. W. and to the Rockefeller Foundation to a grant supporting this work.

Experimental[6]

The Raney nickel used in all experiments was prepared, dried and degassed at 200° as described in previous communications.[4] Three representative experiments are described.

1. **Reaction of Diphenyl Diselenide at 140° with Raney Nickel.**—To a suspension of 65 g. of degassed Raney nickel in xylene, 5.00 g. of diphenyl diselenide[7] was added and the mixture refluxed for 14.5 hr. with continuous stirring. The nickel was then filtered off and washed several times with hot xylene. The combined xylene solutions were then evaporated and the oily residue fractionated *in vacuo*. At 4 mm. there distilled at 125–130° a colorless product which solidified on cooling and after one recrystallization from alcohol melted at 68.5–69.5°. This m.p. was not altered by admixture of authentic diphenyl; yield 0.766 g. A second fraction distilled at 136–142°. The resulting yellowish liquid (0.795 g.) was dissolved in ether, and under cooling 0.3 g. of bromine in ether was added. The mixture was kept in the ice-box with occasional shaking during the first hour. The reaction product was filtered off and recrystallized from carbon disulfide and yielded 1.04 g. (78%) of red needles, which melted at 134° and decomposed at 145° (indicated for $(C_6H_5)_2SeBr_2$: dec. about 148°[8]).

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[1] Paper V of the series "The Action of Raney Nickel on Sulfur Compounds." Presented at the XIV International Congress of Pure and Applied Chemistry, Zurich, July, 1955.

[2] This paper is extracted from a thesis presented to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo by Wolfgang Ferdinand Walter in partial fulfillment of the requirements for the degree of "Dr. em Ciências."

[3] G. E. Wiseman and E. S. Gould, THIS JOURNAL, **76**, 1706 (1954). See also Ng. Ph. Buu-Hoï and Ng. Hoán, *J. Chem. Soc.*, 3745 (1952).

[4] (a) H. Hauptmann and B. Wladislaw, THIS JOURNAL, **72**, 707, 710 (1950); (b) H. Hauptmann, B. Wladislaw, L. L. Nazario and W. F. Walter, *Ann.*, **576**, 45 (1952).

[5] W. F. Walter, Communication to the 4th Meeting of the "Sociedade Brasileira para o Progresso da Ciência," Pôrto Alegre, November, 1952.

[6] All melting points were taken with a Kofler melting point apparatus and are not corrected.

[7] O. Behaghel and H. Seibert, *Ber.*, **65**, 815 (1932).

[8] F. Krafft and R. E. Lyons, *ibid.*, **27**, 1765 (1894).

2. **Reaction of Phenyl Selenobenzoate[9] at 80° with Raney Nickel.**—To a suspension of 35 g. of degassed Raney nickel in benzene was added 1.20 g. of phenyl selenobenzoate. The mixture, protected from light, was refluxed for 15 hr. with continuous stirring. The nickel was extracted several times with hot benzene, the combined benzene solutions evaporated, and the residue distilled *in vacuo*. There was obtained 0.57 g. (yield 54%) of a yellowish liquid, b.p. 135–140° (3 mm.). The liquid was dissolved in ether, cooled and some drops of bromine added. The mixture was left in the ice-box overnight, the reaction product filtered off and recrystallized from carbon disulfide. The red needles obtained decomposed at 145°.

3. **Reaction of Diphenyl Selenide at 180° with Raney Nickel.**—A suspension of 60 g. of Raney nickel in benzene was dried *in vacuo* and then in a nitrogen atmosphere, 6.16 g. of diphenyl selenide was added and a current of nitrogen was then passed over the mixture which was heated at 180° for 8 hr. Then it was extracted thoroughly with benzene; the combined benzene solutions were distilled over a Widmer column and the solid residue fractionated. It boiled at 243–246° and the distillate solidified and melted after recrystallization from alcohol at 69.5–70.5°. This m.p. was not changed by admixture of authentic biphenyl; yield 3.13 g. (77%).

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[9] Prepared by reduction of diphenyl diselenide with glucose (H. Lecher and K. Simon, *ibid.*, **55**, 2423 (1922), and esterification of the resulting selenophenol with benzoyl chloride (H. Rheinboldt and E. Giesbrecht, Bol.n° 129, *Univ. São Paulo, Faculdade Filosofia, Ciências e Letras, Quimica*, n° **3**, 156 (1951); *C. A.*, **46**, 7555e (1952); white needles, m.p. 37.5–38.5°, yield 13% (from the diselenide).

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The Reaction of Ethyl Perfluorobutyrate with Sodium. An Improved Synthesis of Perfluoroheptan-4-one

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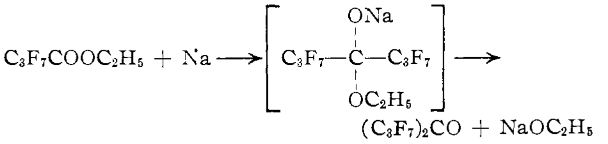
RECEIVED APRIL 18, 1955

The only reported attempts to prepare perfluorinated acyloins were unsuccessful. Ethyl trifluoroacetate reacted with an ethereal solution of metallic sodium to give ethyl γ,γ,γ-trifluoroacetoacetate and polymeric material.[2,3] Since ethyl butyrate is known to undergo the acyloin reaction with much greater facility than ethyl acetate, it was thought that perhaps esters containing the larger perfluoropropyl group might give an acyloin reaction.

Accordingly, a study was made on the reactions of ethyl and methyl perfluoro-*n*-butyrate with sodium. It was quite a surprise to find, however, that this reaction represented the most convenient method yet reported for the synthesis of perfluoroheptan-4-one. The perfluoro ketone was isolated in up to 60% conversion. The known methods for preparing perfluoroheptan-4-one involve the reaction of C_3F_7MgI with C_3F_7COCl or $C_3F_7COOC_2H_5$[4,5] and the reaction of C_3F_7Li with $C_3F_7COOC_2H_5$.[6] The highest yield reported was 31%.[5] The distinct advantage of the present method is that, in addition to improved yields, it does not involve the critically precise conditions necessary for the preparation of perfluoropropylmagnesium iodide. The synthesis of perfluoroheptan-4-one now can be carried out with commercially available reactants.

The precise stoichiometry of the reaction of the esters of perfluorobutyric acid with sodium could not be ascertained. The perfluoro ketone is not formed until after the reaction mixture is acidified. The initial product is undoubtedly a sodium salt.



$$C_3F_7COOC_2H_5 + Na \longrightarrow \left[C_3F_7-\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{\overset{|}{\underset{|}{C}}}}-C_3F_7 \right] \longrightarrow (C_3F_7)_2CO + NaOC_2H_5$$

Some side reaction or decomposition with loss of fluoride ion was observed in all runs. It was noted also in most of the experiments conducted that a small fraction boiling slightly above 100° gave a bright-red coloration (in the organic layer) with ferric chloride solution, which may indicate the presence of traces of a perfluorinated ene-diol. The highest yields of ketone were obtained when the reaction was carried out at room temperature. At higher temperatures two unidentified higher boiling fractions were produced.

Two unsuccessful attempts were made to prepare the perfluorinated acyloin by slightly modified routes. From the reaction of the acid chloride and sodium[7] in ether, the perfluorobutyric acid etherate, $2C_3F_7COOH \cdot (C_2H_5)_2O$,[8] was the product isolated. The reaction of ethyl perfluorobutyrate with sodium in liquid ammonia at −50° did not give any acyloin despite the fact that this method was quite successful for the preparation of aliphatic acyloins.[9] The sole product isolated was perfluorobutyramide.

Little is known about the chemistry of perfluoroheptan-4-one. The tendency of fluorinated ketones to form hydrates has been noted before,[5,10,11] but the pure hydrates have not been obtained. Fukuhara and Bigelow[10] observed that hexafluoroacetone was soluble in water but was completely volatile at low pressures. The slightly water-soluble crystalline hydrate of perfluoroheptan-4-one, m.p. 35–35.5°, which is only slightly volatile *in vacuo*, now has been isolated, and the dihydroxy structure, *i.e.*, perfluoroheptane-4,4-diol, was characterized by elemental analysis and infrared spectral examination.

Perfluoroheptane-4,4-diol was found to form a 1:1 adduct with several tertiary aliphatic amines. The triethylamine adduct, m.p. 88°, was very stable and could be sublimed at 100° at atmospheric pressure. A solid adduct also was obtained

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[1b] Based on a portion of the thesis presented by R. A. Braun to Temple University in partial fulfillment of the requirement for the Masters degree.

[2] E. T. McBee, O. R. Pierce, *et al.*, THIS JOURNAL, **75**, 4090 (1953).

[3] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

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[8] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5139 (1951).

[9] M. S. Kharasch, *J. Org. Chem.*, **5**, 362 (1940).

[10] N. Fukuhara and L. A. Bigelow, THIS JOURNAL, **63**, 788 (1941).

[11] A. L. Henne, *ibid.*, **72**, 3577 (1950).